THERMODYNAMICS OF THE SYSTEM WATER-VAPOR CELLULOSE

BY

MATTHEW A. DZIECIUCH
B.Sc.

1958

THESIS
1958 F
#5

Ex libris
universitatis
albertaensis

UNIVERSITY OF ALBERTA
QUAECUMQUE VERA

Thesis
1958 (F)
#5

THE UNIVERSITY OF ALBERTA

THERMODYNAMICS OF THE CELLULOSE - WATER VAPOUR SYSTEM

A DISSERTATION
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE.

DEPARTMENT OF CHEMISTRY

by

MATTHEW A. DZIECIUCH

EDMONTON, ALBERTA

JUNE 16, 1958

Digitized by the Internet Archive
in 2017 with funding from
University of Alberta Libraries

https://archive.org/details/dzieciuch1958

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. L. Morrison for his constant interest, valuable guidance and unfailing cooperation during the course of this investigation.

Acknowledgement is also made to the National Research Council for grants in aid of the work done in the summer of 1957 and the winter of 1957-58.

Table of Contents

	Page
List of Tables	
List of Figures	
Introduction	1
Chemical and Physical Properties of Cellulose	5
Sample Preparation and Determination of the Isotherm	6
Apparatus and Experimental Method	7
Results and Calculations	10
Heat of Wetting	10
Heat of Sorption and Free Energy of Sorption	13 - 15
Entropy Changes	18
Adsorption Areas	19
Discussion of Results	20
Experimental Errors	27

List of Tables

		Page
Table I	Heats of Wetting	10
Table II	Heats of Adsorption	14
Table III	The Sorption Isotherm	16
Table IV	Free Energy of Sorption	17
Table V	Entropy Changes	18
Table VI	Monolayer Contents	19

List of Figures

		Page
Figure 1	Sample Cell	ff 7
Figure 2	Experimental Curves	ff 8
Figure 3	Heat of Wetting	ff 12
Figure 4	The Sorption Isotherm	ff 16
Figure 5	Integral Thermodynamic Properties	ff 18
Figure 6	Differential Thermodynamic Properties	ff 18
Figure 7	B.E.T. and H.J.	ff 19
Figure 8	Radial Swelling	ff 25

Introduction

This investigation is part of a larger project on the mass and energy relationships of water vapour and fibrous gel systems. (1,2,3,4,5).

The purpose of this investigation was to measure the heats of wetting of cellulose by water through the use of calorimetric techniques. This data, for samples with varying moisture contents, from zero moisture content to saturation together with data from water vapour sorption isotherms permits the calculation of certain thermodynamic functions for the sorption process.

From the heats of wetting, the net integral heat of adsorption may be obtained experimentally. The differential heat of adsorption, $\overline{\Delta H}$, is of theoretical importance, since this gives the partial molal heat at every water content over the range studied. The heat of wetting, from which the integral heat of adsorption is obtained, is measured experimentally and is defined as the heat evolved when the material at a given moisture content, x, is completely wetted. It is expressed in calories per 100 grams of the dry material.

The differential heat of sorption, $\overline{\Delta H}$, is the heat evolved when one mole of water is adsorbed by an infinite mass of material. The differential free energy, $\overline{\Delta F}$, is defined as the change in free energy occuring when one mole of

water is added to an infinite mass of cellulose at constant temperature and pressure and ΔS is the net entropy change in excess of the entropy of condensation of water vapour to liquid water.

The thermodynamic functions are calculated by using Bull's (6) equation as modified by Dole and McLaren (7).

Previous work on this system has been done by Argue and Maass (1,8), who measured the heat of wetting of dry and partially saturated cellulose over the range 0-8% water content. Their cellulose samples were prepared by drying in air at 100°C, then allowing the sample to adsorb moisture from an atmosphere containing a definite amount of water vapour. The desorbed samples were prepared by heating a saturated sample at 50°C over phosphorous pentoxide until the desired amount of water vapour was left on the sample. They measured the heats of wetting in a rotating adiabatic calorimeter, and the subsequent temperature rise by means of a platinum resistance thermometer with a Mueller bridge.

Wahba (9,10) also measured the heats of wetting of cellulose. Samples were prepared by evacuation for a period of 15 hours at 65°C. Heats of wetting were then obtained by employing a Dewar flask and a Beckmann thermometer. The temperature rise was electrically duplicated to obtain the heat of wetting.

The sorption isotherm was obtained by using a spring

balance in an evacuated system, into which desired amounts of water vapour were admitted, and the amount of water vapour adsorbed was then determined gravimetrically.

Heats of wetting as obtained by Argue and Maass (8) and Wahba (9,10) show hysteresis in the sorption cycle. However, previous work in this laboratory on wool fibroin (1,2) showed that there was no hysteresis in the heats of wetting. The present work included a revised procedure for sample preparation, described in a later paragraph, to reduce the possibilities of a pseudo-hysteresis phenomenon. The well-known observation of hysteresis in the sorption isotherms, taken along with the absence of hysteresis in the enthalpies suggests that the hysteresis is an entropy phenomenon.

This observation supports the explanation given by Barkas (11) that hysteresis in the sorption isotherms of fibrous materials is due to their plastic rather than their elastic nature.

A review of the literature on the integral and differential heats of sorption of water by cellulose is given by Rees (12) and Gutherie (13). In their papers values from calorimetric methods and values calculated from adsorption measurements by the Clausius-Clapeyron equation are given. Since this is only an indirect calculation based on two isotherms, the results are uncertain especially at high and low ranges of water content.

In this present investigation previous work (8,9,12,13, 14,15) has been extended on cellulose and the integral and differential heats of sorption, entropy and the free energy have been evaluated from zero moisture content to saturation.

Calculations based on application of the Brunauer, Emmett and Teller and the Harkins-Jura equations to the sorption isotherms can be of assistance in interpreting the thermodynamic data. Dunford and Morrison (4) showed that the Harkins-Jura equation which fitted the upper part of the adsorption isotherm gave the same monolayer content as the Brunauer, Emmett and Teller equation which fits the lower part (Bull 6). They considered that, after a monolayer of water was adsorbed, no new sites were developed in the gel, and that the remaining water was adsorbed on top of the monolayer. It is already known that the same calculations apply to cellulose (2,9,10); they are being applied to the samples used in this work.

Some Chemical and Physical Properties of Cellulose (16)

Cellulose is considered to be a neutral hydroxylic molecule composed of 2000-3000 β-glucoside units, with an average molecular weight between 300,000-500,000.

The fibres show crystalline regions that are explained on the basis of the micellar theory; this postulates that the crystalline supermolecular unit is made up of parallel oriented chains (micelles). The ideal cellulose molecule is a linear polymer composed of individual anhydroglucose units linked at the 1 and 4 positions through glucosidic bonds with the β-configuration. The flat shape of the rings and the spatial distribution of the hydroxyl groups appears to favour the formation of ribbon-shaped laterally ordered sheets.

The behaviour of cellulose is modified by the nature of its solid state. It is neither completely crystalline like glucose nor amorphous like a super-cooled liquid, but has some aspects of both states. As a result, no two cellulose fibres have exactly the same internal structure; each reflects its individual history.

The sorption of water is supposed to occur by bonding to the hydroxyl groups present in the amorphous regions of the cellulose molecular structure, that is, in the intermicellar spaces (18). The heat of wetting probably depends on the availability of such hydroxyl groups. In particular, the differential entholpies should permit one to get a measure of hydrogen bond values for water on cellulose (2).

Sample Preparation and Determination of the Isotherm

The samples were prepared and the adsorption-desorption isotherm were determined in an apparatus originally designed by Wiig and Juhola for charcoal-water isotherms (17).

About 1 gram of cellulose was placed in the lower compartment of the sample cell, a weighed stopcock was sealed to this compartment and the assembly was evacuated at room temperature for a minimum of 24 hours by means of mercury diffusion and oil pumps. The dry weight of the cellulose was then obtained by weighing the assembly after carefully removing the grease (Apiezon L) from the ground glass joint with ether.

Water vapour was added up to a desired amount, for adsorption experiments, the sample was saturated with water vapour, left for 24 hours and then desorbed by evacuation to the desired water content. In all cases, at least 24 hours elapsed between the establishment of the final water content and the heat of wetting experiment.

The sorption isotherm was determined on an 8 gram sample using an oil manometer (Apiezon B) at 24.6°C. Each point was allowed 24 hours for equilibration. Special precautions had to be taken near the saturation region because the interface of the water bath thermostat had a slightly lower temperature than the bulk of the water. A small heater was clasped around the tubes of the cell and of the water reservoir at this interface to overcome the cool spots.

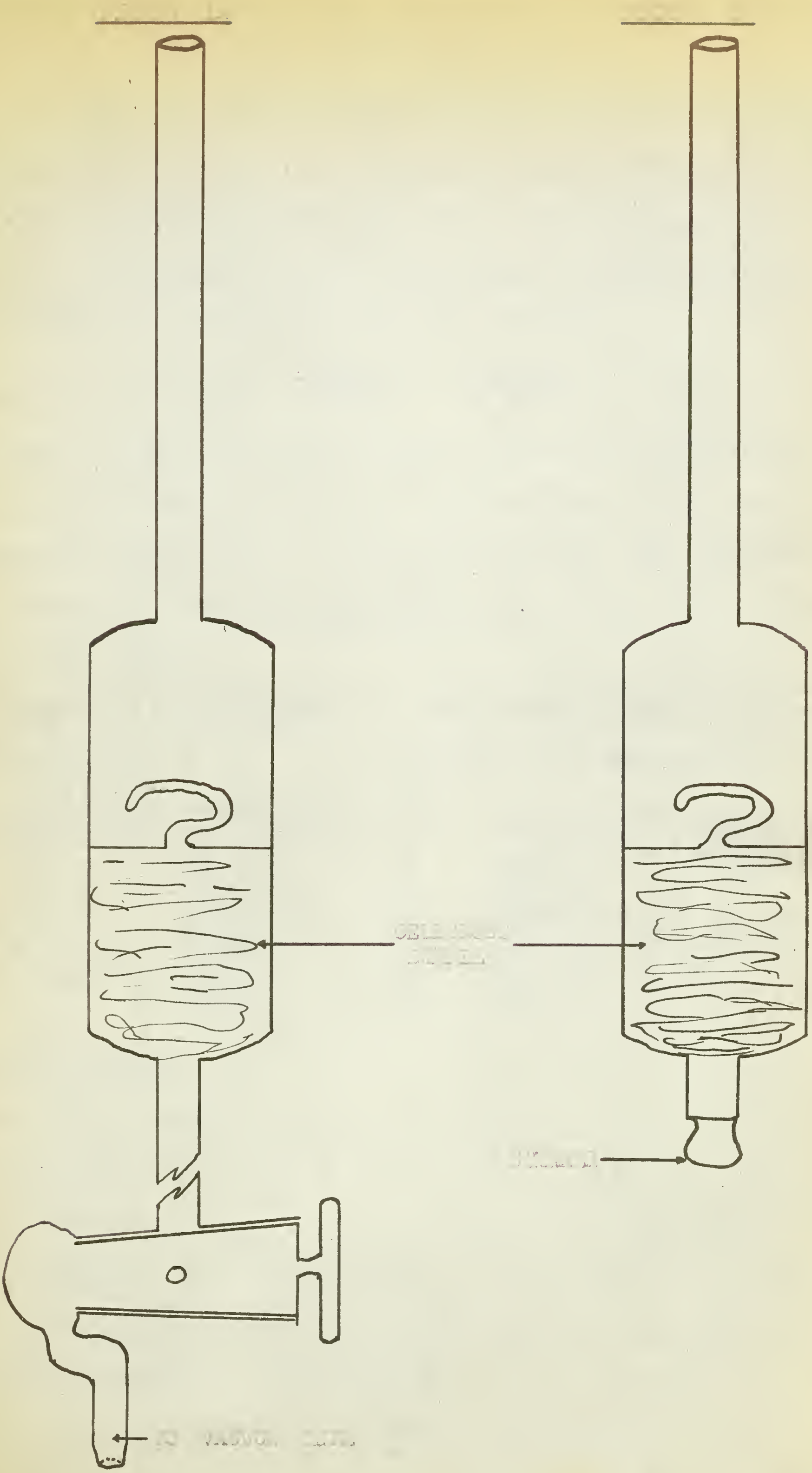
Apparatus and Experimental Procedure

The details of construction of the calorimeter and the experimental procedure have been described by Hanlan (1).

The sample cell was modified slightly; a small paddle stirrer was made on the bottom of the cell, when it was removed from the vacuum line. (Fig.1A). The completed cell is shown in Figure 1B.

The stirrer insured a rapid, and uniform distribution of heat and decreased the time lag of temperature distribution.

Briefly, a carefully conditioned sample is equilibrated for at least twenty-four hours in a thermostatted calorimeter. The sample is then wetted in its sealed sample tube, by letting water rush into the evacuated cell whereby a quick contact between solid and the liquid is assured without the interference of entrapped air. The resulting change in temperature is noted by a thermistor used as the unknown resistance of a Wheatstone bridge circuit, and simultaneously recorded by a Sargent recorder, model S-72150, with a sensitivity of 0.1% or 20μV whichever the greater. Readings were taken until no further change in resistance (temperature) was detected. This required approximately one hour. The apparatus was then allowed to re-equilibrate and the temperature rise duplicated electrically, again using the Wheatstone Bridge circuit in conjunction with the recorder until no further change in resistance could be detected.


[illegible]
[illegible]
CELLOPHANE
[illegible]
[illegible]
TO VACUUM LINE

The time of electrical heating necessary to exactly duplicate the rise in temperature due to wetting can be read directly from the graph recorded. Since equal temperature rises correspond to equal evolutions of heat, the heat of wetting was calculated using the formula:

$$\text{Heat in calories} = \frac{I^2Rt}{4.183} = \frac{V_1V_2t}{R_s 4.183}$$

where V_1 and V_2 are the drops in potential across the heating coil and standard resistance during time, t, of electrical heating, and R_s the standard resistance. The following is a sample run, showing the graphs, (see Fig. 2) and calculations used.

Sample 95D (1.62% H_2O)   Room temperature= 21.2°C

a) Wetting   b) Electrical Duplication

Time (sec's)	Resistance	Time	Resistance	Potential	
min				heater	std.Res.
0	3090.9	0	3090.8	.6084 ✓	.6315 ✓
3	3090.9	3	3090.8		
5	3090.9	5	3090.8		
60	3084.4	45	3082.4	t= 410.3 secs.	
65	3084.4	50	3082.4		
70	3084.4	55	3082.4		

Calculations-

t= 410.3 sec's

V_1= .6084 x 5

V_2= .6315 x 5

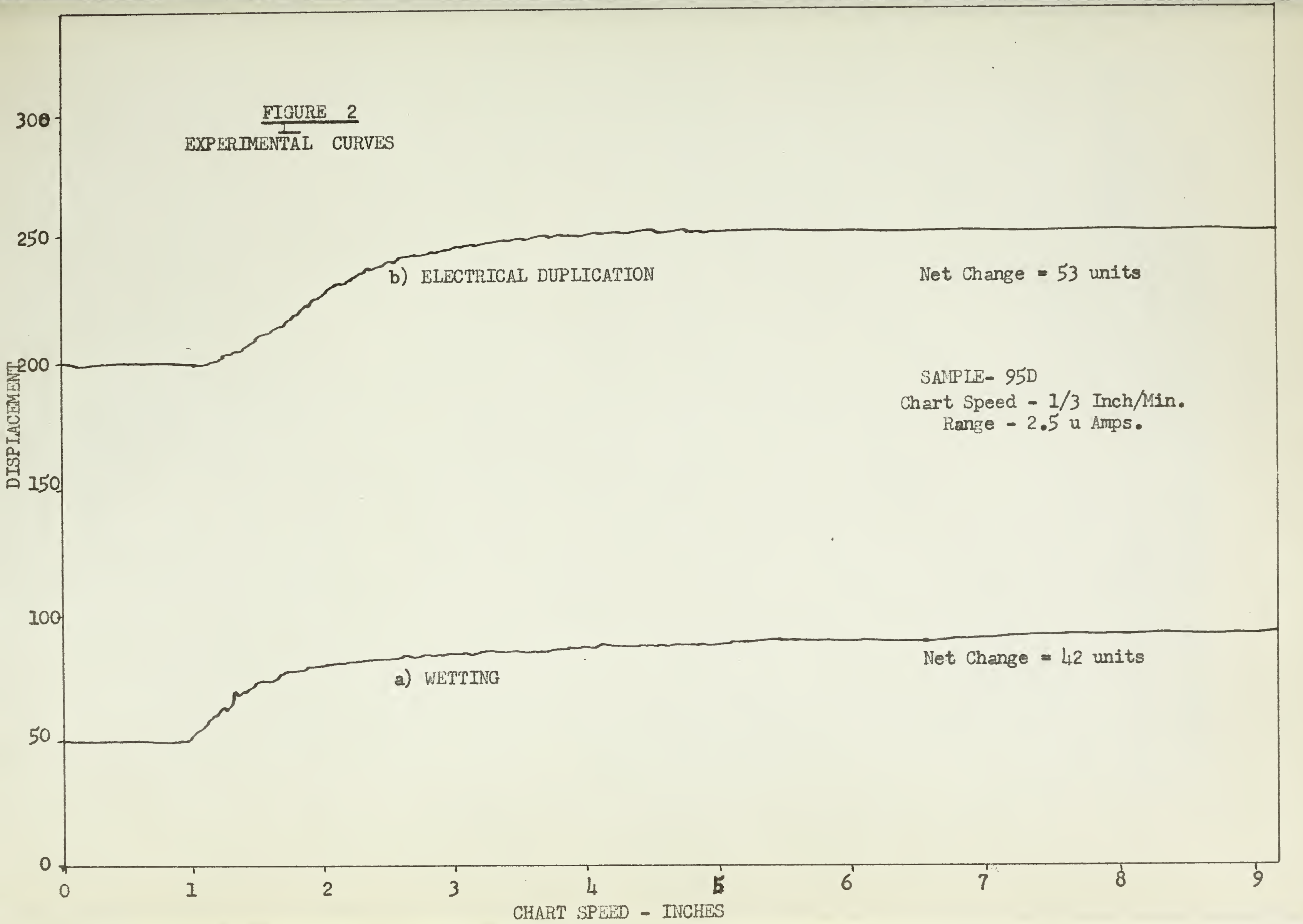
R_s= 99.91

Electrical heat= 9.43 calories

Sample weight= 1.0013 gms.

Heat of wetting= 7.28 cal/gm

FIGURE 2
EXPERIMENTAL CURVES



At the end of a run, the used sample was removed, a new sample installed and allowed to equilibrate at 24.5°C for 24 hours.

Results and Calculations

Heats of Wetting

The heats of wetting of standard cellulose, with varying water contents, both adsorbed and desorbed, are given in Table 1 and Figure 3.

The results of Argue and Maass (8) and Wahba (9,10) are included.

The water content is given in percent of the dry weight of cellulose. The heats of wetting are given in calories per gram of dry cellulose.

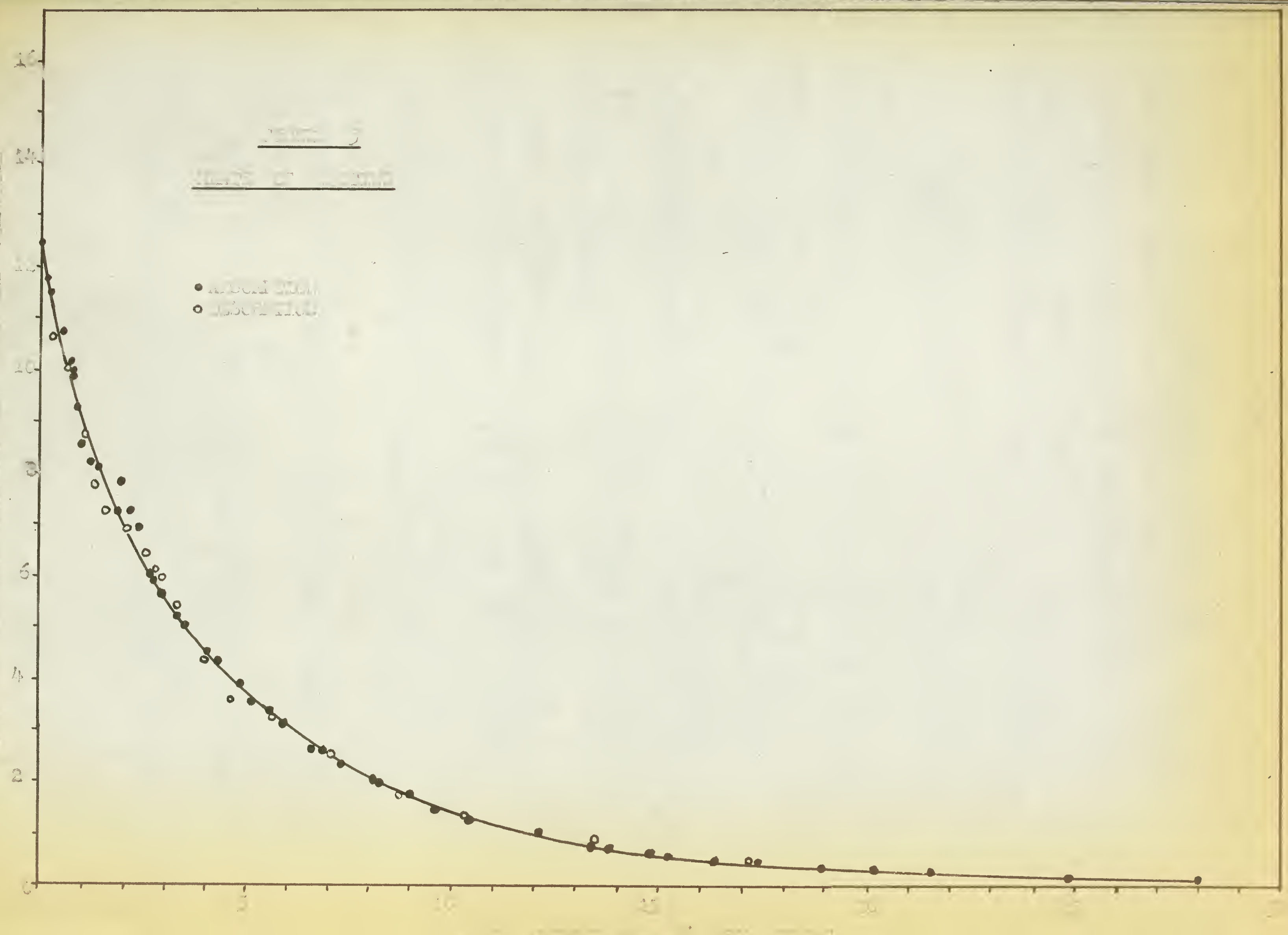
There is a slight scatter in the heats of wetting for samples to approximately three percent moisture content. This we feel is due sample preparation and the difficulty in removing the last traces of water from the cellulose rather than to calorimetric measurements.

Table 1

Water Content %		Heats of Wetting. Cal/gm Dry Cellulose		
Adsorbed	Desorbed	Our Values	Wahba	Argue and Maass
0		12.43		
0		12.51		
0		12.49	10.72	10.16
.17		11.76		
.29		11.45	10.18	9.48
.55		10.71	9.52	8.91
.77		10.12	8.88	8.45
.878		9.36		
1.052		8.55	8.35	7.98
1.28		8.21		
1.45		8.20		
1.95		7.23	6.45	6.33
2.056		7.82		
2.20		7.365	6.10	5.98
2.35		6.95		

Water Content %		Heats of Wetting	Cal/gm Dry Cellulose	
Adsorbed	Desorbed	Our Values	Wahba	Argue and Maass
2.72		6.08	5.38	5.19
2.73		5.89		
2.97		5.61	5.05	4.95
3.46		5.23		
3.60		5.05	4.28	4.09
4.12		4.56		
4.40		4.40	3.52	3.40
4.98		3.85		
5.13		3.49		
5.59		3.39	2.68	2.58
5.97		3.17		
6.66		2.62	2.19	2.02
6.89		2.64		
7.36		2.33		
8.14		2.03		
8.15		1.95	1.71	1.59
8.70		1.68		
8.88		1.36		
9.00		1.88	1.32	
9.67		1.46		
10.44		1.32		
12.13		1.07		
13.31		.89		
13.48		.806		
13.75		.76		
14.78		.63		
15.20		.60		
16.36		.48		
17.28		.57		
18.94		.397		
19.79		.394		
20.28		.357		
21.51		.38		
24.67		.183		
28.43		.101		
33.31		0		
35.59		0		
	0.35	10.65		8.85
	0.74	10.04		
	1.17	8.74		8.41
	1.38	7.77		
	1.62	7.28	7.71	7.91
	2.20	6.93	6.61	6.69
	2.61	6.48		
	2.81	6.05		
	3.00	5.95	5.45	5.30
	3.38	5.40		

Water Content %		Heats of Wetting Cal/gm Dry Cellulose		
Adsorbed	Desorbed	Our Values	Wahba	Argue and Maass
	4.01	4.33	4.33	4.02
	4.67	3.55		
	5.67	3.38	3.01	2.75
	7.11	2.54	2.28	
	8.76	1.71		
	10.37	1.34	1.34	
	13.40	0.88		
	17.20	0.49		



16
14
12
10
8
6
4
2
0
5
10
15
20
25
30

Heat of Adsorption, ΔH and $\overline{\Delta H}$

Using the method of Dole and McLaren (7), slightly modified, the net integral heats of adsorption, ΔH in calories per 100 gm of cellulose, (above the heat of condensation of water vapour to liquid), have been calculated.

In our experiments the heat of wetting, q_0, with excess liquid water, of 100 gram of dry cellulose is evolved by process 1.

1) Cellulose (dry at $p = o$) $+$ excess liquid H_2O (at P_0) = cellulose (with excess liquid **H2O** at P_0) $+$ $q_0$cal.

where P_0 is the vapour pressure of pure water at 25°C.

The heat of wetting, q, by excess liquid H_2O, of 100 gram of cellulose which has been equilibrated at a pressure equal to P with n moles of H_2O (adsorbed or desorbed) is given by process 2.

2) Cellulose (with n H_2O at p) $+$ excess liquid H_2O (at P_0) = cellulose (with excess liquid H_2O at P_0) $+$ q calories.

The net integral heat of adsorption, $\Delta H = q_0 - q$, is obtained by subtracting process 2 from process 1 giving process 3.

3)Cellulose (dry at $P = 0$) $+$ n H_2O (at P_0) = Cellulose (with n H_2O at P) $+$ ΔH.

The values for ΔH, given in calories per 100 gm of dry cellulose are shown in Table 2 and Figure 5.

The differential heats of adsorption, $\overline{\Delta H}$, that is the

partial molal heats of adsorption (see figure 6 and table 2) were obtained by graphical and tabular differentiation of ΔH versus n.(25) This corresponds to the heat of adsorption of one mole of water on an infinite amount of cellulose.

Table 2

Heat of Adsorption of Water on Cellulose

n moles of H_2O per 100 gm. Cellulose	Heat of Wetting Cal/100 gm. Cellulose	ΔH Cal/100 gm Cellulose	$-\overline{\Delta H} = \frac{\partial(\Delta H)}{\partial n}$
0	1237	0	7940
.05	937	300	4700
.10	737	500	3300
.15	597	640	2235
.20	499	738	1680
.25	417	820	1430
.30	345	892	1310
.35	278	959	1095
.40	215	1012	855
.45	187	1050	680
.50	157	1080	540
.55	137	1100	410
.60	117	1120	320
.65	99	1138	255
.70	85	1152	205
.75	72	1165	165
.80	60	1177	140
.90	47	1190	105
1.00	37	1200	80
1.10	27	1210	65
1.20	22	1215	50
1.30	17	1220	40
1.40	7	1230	35
1.50	0	1237	30

The integral and differential free energies, ΔF and $\overline{\Delta F}$, for the isothermal adsorption process, were calculated from the water vapour adsorption isotherm obtained by Dr. Morrison (Table 3, Figure 4).

The Free Energy of Adsorption

Originally, Bull (6) using the equation,

$$\Delta F = -\frac{RT}{M}\int_0^x \frac{a}{x}\,dx$$

where M= molecular weight of H_2O

a= grams of H_2O adsorbed

x= P/P_0= partial pressure of H_2O at the absolute temperature T.

calculated the free energy changes for the adsorption of water vapour on a number of proteins. Dole and McLaren (7) working from the general equation for dF, showed that the integral free energy change, ΔF, for our process 3 involves the inclusion of the term $nRT\ln x$

Thus,

$$\Delta F = -\frac{RT}{M}\int_0^x \frac{a}{x}\,dx + nRT\ln x$$

where R= the gas constant = 1.937 cal/mole degree

T= the absolute temperature

n= the number of moles of water adsorbed

a= grams of water adsorbed

M= molecular weight of pure water.

This integral was evaluated graphically by plotting a/x Vs. x.

The differential free energy changes were calculated for the adsorption and desorption branches of the isotherm, using the formula given by Dole and McLaren (7).

$$\overline{\Delta F} = \frac{\partial(\Delta F)}{\partial n} = RT \ln x.$$

The values calculated for ΔF and $\overline{\Delta F}$ are given in Table 4 and Figures 5 and 6 respectively. The subscripts 1 and 2 refer to the values for adsorption and desorption respectively.

Table 3

Adsorption- Desorption Isotherm

$x = P/P_0$	Adsorption gm H_2O/100 gm Cellulose	Desorption gm H_2O/100 gm Cellulose
.005	0.38	0.39
.01	0.57	0.58
.02	0.90	0.93
.03	1.12	1.14
.04	1.33	1.47
.05	1.49	1.57
.10	2.12	2.35
.15	2.66	2.99
.20	3.13	3.50
.25	3.55	3.95
.30	3.91	4.43
.35	4.30	4.92
.40	4.72	5.48
.45	5.13	5.99
.50	5.56	6.52
.55	6.07	7.11
.60	6.61	7.71
.65	7.22	8.38
.70	7.90	9.11
.75	8.71	9.97
.80	9.68	10.95
.85	10.87	12.15
.90	12.60	13.85
.95	15.12	16.35
1.00	23.00	23.00

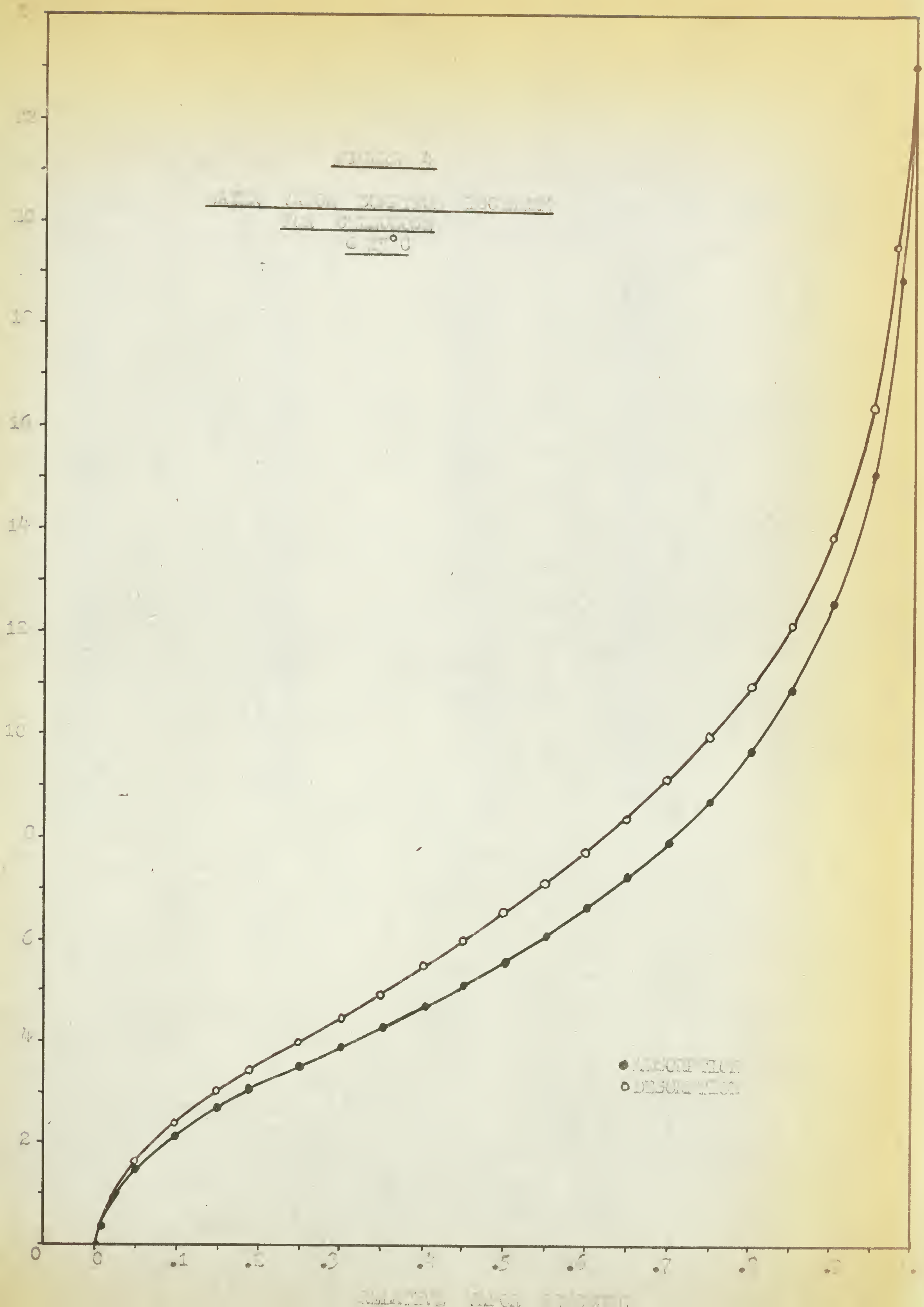
0
2
4
6
8
10
12
14
16
18
20
22
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.
● ADSORPTION
○ DESORPTION
RELATIVE [illegible] PRESSURE

FIGURE [illegible]

[illegible]
[illegible]
[illegible]°C

Table 4

Integral and Differential Free Energies

n moles H_2O	$-\Delta F_1$ cal	$-\overline{\Delta F_1}$ cal	$-\Delta F_2$ cal	$-\overline{\Delta F_2}$ cal
		per 100 gm cellulose		
.05	155	2340	155	2550
.075	210	1910	210	2060
.10	255	1570	265	1720
.15	320	1100	340	1220
.20	365	795	380	910
.25	398	565	430	700
.30	425	420	465	550
.35	445	340	485	435
.40	460	265	505	360
.45	470	205	520	275
.50	480	160	530	215
.55	485	125	545	170
.60	490	105	550	135
.65	495	80	555	110
.70	500	70	560	85
.75	502	50	565	70
.80	505	40	568	60
.85	507	30	570	50
.90	508	25	571	45
.95	509	20	572	35
1.00	509	18	573	30
1.05	510	15	575	25
1.10	511	10	578	20
1.15	511	8	580	15
1.20	512	5	581	8
1.25		3		3

Entropy Changes in Adsorption

The integral and differential entropy changes are given by,

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

$$\overline{\Delta S} = \frac{\overline{\Delta H} - \overline{\Delta F}}{T}$$

The values for ΔS are given in Table 5 and Figure 5; $\overline{\Delta S}$ in Table 5 and Figure 6. Values for adsorption and desorption are again indicated by the subscripts 1 and 2 respectively.

Table 5

Integral and Differential Entropy Changes

n.moles of H_2O	$-\Delta S_1$ e.u.	$-\Delta S_2$ e.u.	$-\overline{\Delta S}_1$ e.u.	$-\overline{\Delta S}_2$ e.u.
.05	.45	.43		
.075	.65	.58		
.10	.82	.75	5.80	5.30
.15	1.07	.97	3.81	3.47
.20	1.25	1.14	2.97	2.58
.25	1.44	1.22	2.90	2.45
.30	1.57	1.45	2.99	2.55
.35	1.73	1.59	2.63	2.21
.40	1.85	1.85	2.13	1.66
.45	1.95	1.79	1.59	1.36
.50	2.01	1.85	1.27	1.09
.55	2.06	1.86	.96	.81
.60	2.11	1.91	.72	.62
.65	2.16	1.96	.59	.49
.70	2.19	1.99	.49	.40
.80	2.26	2.04	.34	.27
.90	2.29	2.08	.27	.18
1.00	2.32	2.10	.21	.17
1.10	2.35	2.12	.18	.16
1.20	2.36	2.13	.15	.15

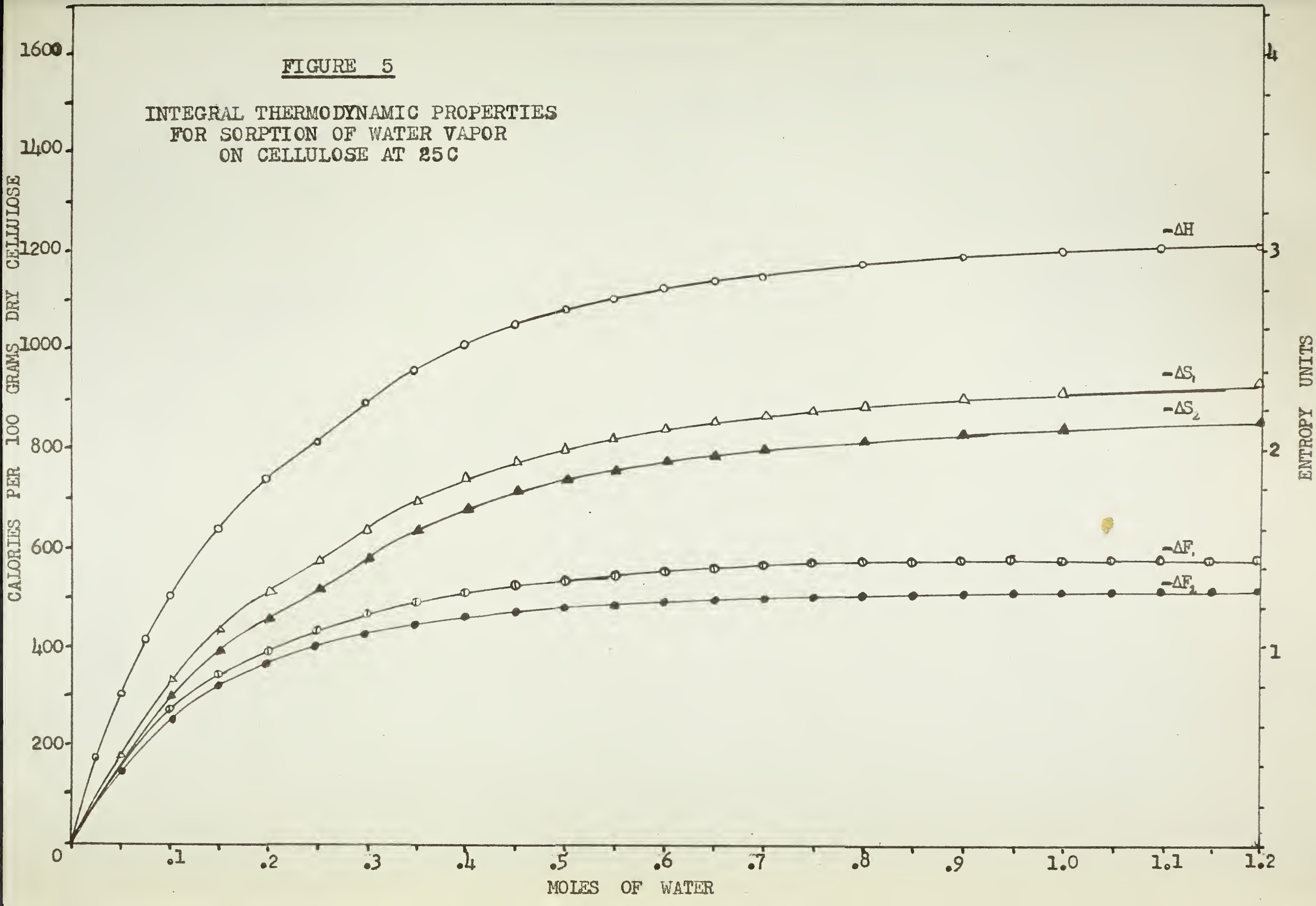
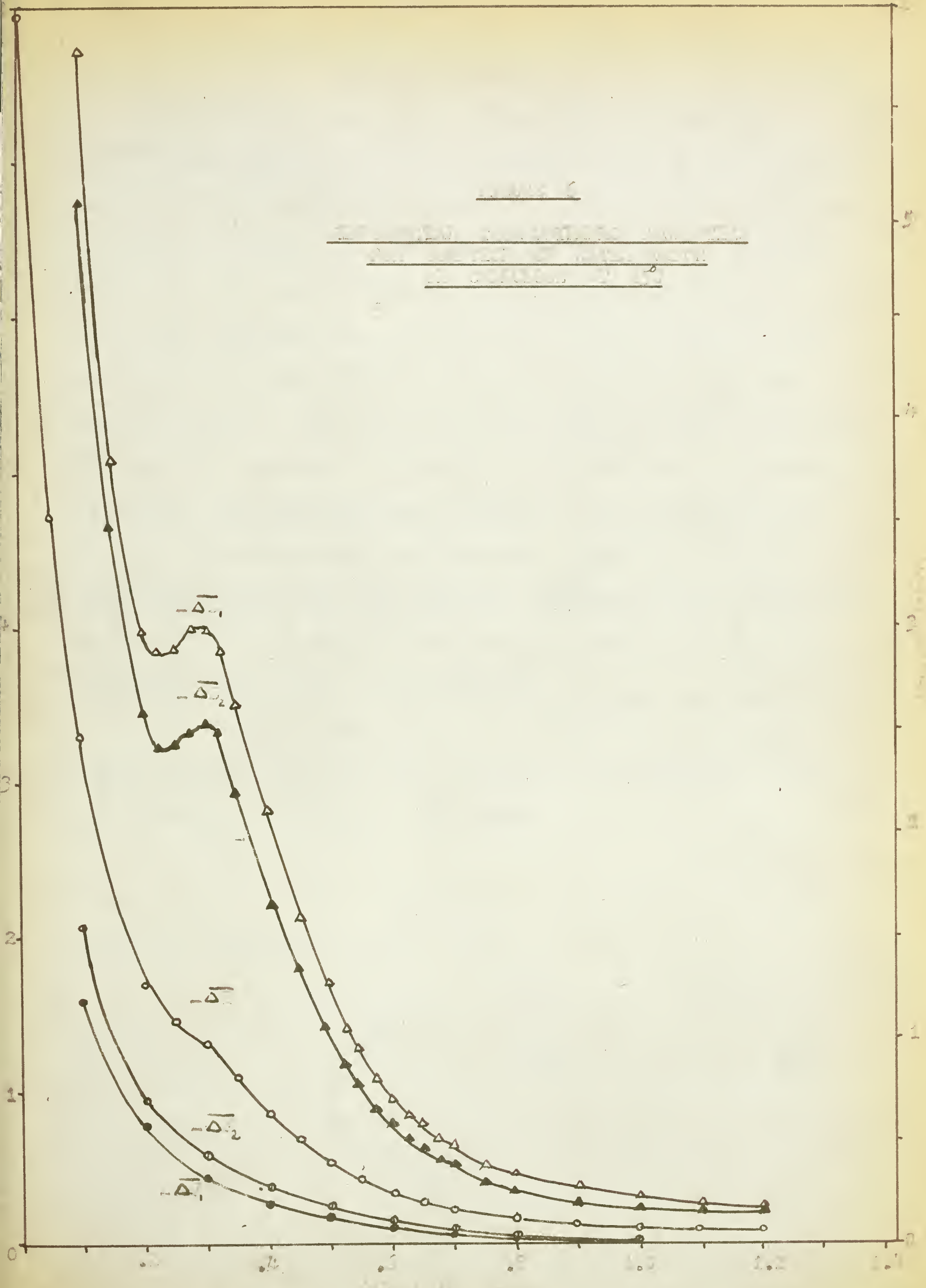


FIGURE 5

INTEGRAL THERMODYNAMIC PROPERTIES
FOR SORPTION OF WATER VAPOR
ON CELLULOSE AT 25C



-Δ₁
-Δ₂
-Δ
-Δ₂
-Δ₁
0
1
2
3
4
.2
.4
.6
.8
1.0
1.2
1.4
0
1
2
3
4
5

[illegible]

[illegible]
[illegible]
[illegible]

Adsorption Areas

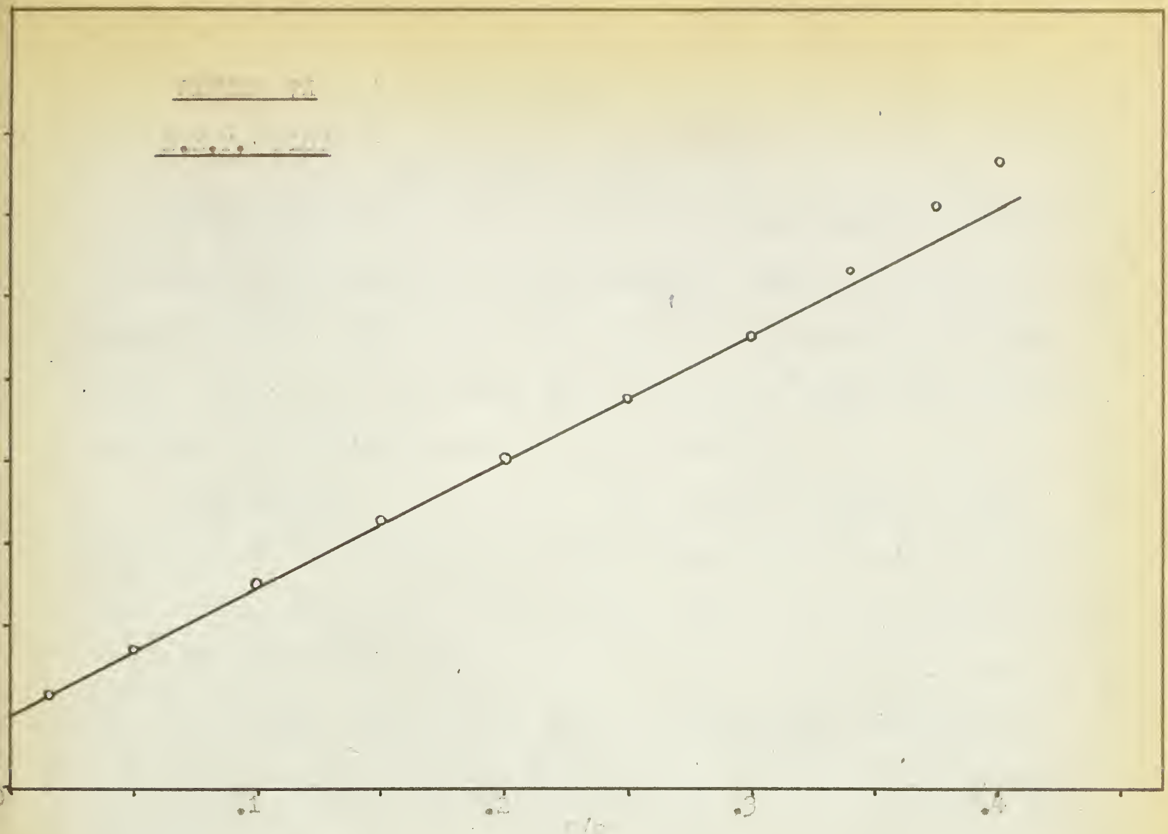
The Brunauer, Emmett and Teller (19) plot of the adsorption isotherm is given in Figure 7A and a plot of the adsorption data according to the Harkins-Jura (20) equation is given in Figure 7B. The monolayer contents calculated from these two equations are 3.05 and 3.07 gm H_2O/100 gm cellulose respectively. It has been shown by Dunford and Morrison (4), that, though these two equations apply to opposite ends of the adsorption isotherms of water vapour on proteins as measured by Bull (6), they give within experimental error, the same monolayer content. For the adsorption isotherm on cellulose, the Brunauer, Emmett and Teller equation applies over the relative pressure range of x= 0.075 to x= .37 and the Harkins-Jura equation over the relative pressure range of x= .60 to x= 1.00.

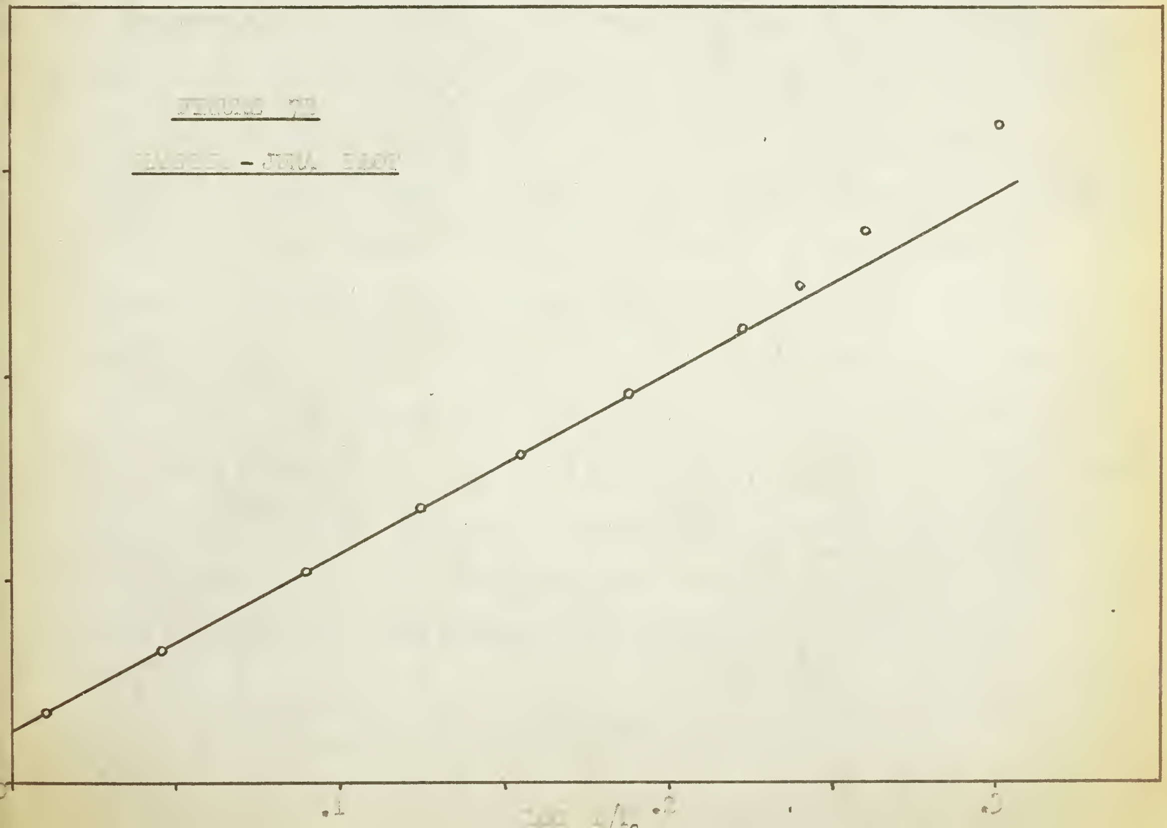
Table 6 shows the monolayer contents for cellulose from our isotherm, and those calculated from Wahba's (9,10) and Urquart and Williams' (21) data.

Table 6

Monolayer Contents for Cellulose

	Our Values	Wahba	Urquart and Williams
B.E.T.	3.05	3.080	3.38
H-J	3.07	3.035	3.60


0
.1
.2
.3
.4


0
.1
.2
.3

Discussion of Results

The heat of wetting values which were obtained (Table 1 and Figure 3) are considerably higher, especially at low water content, than those of Argue and Maass (8) and Wahba (10). Also, no hysteresis was observed between the heats of wetting for adsorbed and desorbed samples.

The scatter of values in the initial portion of the curve could be attributed to the "zippering" effect (3,8,30) and to the high activation energy requirements necessary to transfer the water uniformly into the micellar structure of the cellulose. The scatter could probably be reduced by using smaller samples and by allowing a longer time of evacuation.

Comparing our calculated thermodynamic functions with those obtained by Wahba (10) and Guthrie (13), we note that our values for the integral and differential heats and entropies reach higher values. Also, differential enthalpies, $-\overline{\Delta}H$, of Wahba and of Guthrie show no discontinuities, whereas ours shows very characteristic ones. The differential entropy, $-\overline{\Delta}S$ as found by Wahba shows a rapid increase in the initial stages which is quite different from ours and that of Guthrie. Wahba's interpretation of his results does n take into account the highly perturbed state of the adsorbent, especially in the low water content range. Guthrie's (13) differential entropy curve does decrease with increasing

moisture like ours but does not have the discontinuities which are observed in our differential entropy curve.

The differential heat of adsorption, $-\overline{\Delta H}$, (Figure 6 Table 2) curve shows a discontinuity which coincides with the limit of the B.E.T. monolayer range. This discontinuity is interpreted in terms of hydrogen bonding. Thus if we assume an energy of 4.5 K cal. per hydrogen bond in liquid water, and that each molecule of water makes one bond, then we obtain a hydrogen bond energy of 5.9 K cal. per mole of water.

From this point ($n = .32$) the $-\overline{\Delta H}$ curve continually decreases as less and less tightly bound water continues to adsorb on the cellulose, finally reaching very low values at saturation when the successive layers become indistinguishable from the liquid water.

The high initial values of the $-\overline{\Delta S}$ (Figure 6,Table 5) at low water content are comparable to the entropy of freezing of water (5.4 e.u. at 30°C.) as pointed out by Davis and McLaren (25). This supports the hypothesis of tightly bound chemisorbed water as postulated by Pauling (23) and Cassie (26).

The initial large drop in $-\overline{\Delta S}$ (and in $-\overline{\Delta H}$) is attributed partly to the high degree of disorganization of the cellulose structure, and partly to a transition from a

situation in which each water molecule forms 2 hydrogen bonds to that in which it forms one hydrogen bond. The ordering effect of adsorbing water eventually becomes more important and results in a minimum at about $n = 0.2$ in the net $-\overline{\Delta S}$. It is interesting to note that this recovery occurs in a range which coincides with the range over which the B.E.T. equation applies. Beyond this minimum the $-\overline{\Delta S}$ curve rises to a maximum. In this range it is considered that adsorption is largely a phenomenon affecting the adsorbate water; and that the adsorbent cellulose is itself not changing very much. In this region ($n = 0.2$-0.3) the monolayer is completed. The adsorption of the second and successive layers then continues, this occurs with less organization, and so $-\overline{\Delta S}$ decreases again, until, with the formation of a sufficient number of layers, the water film becomes mobile.

The evidence for the onset of a mobile condensed film is (1) the lower limit of the H.J. equation, range is $n = 0.6$ (2) a discontinuity in the differential enthalpy and entropy curves occurs at $n = 0.7$.

The H.J. equation applies to condensed mobile films (20,4). The transition from an immobile to a mobile film should involve an increase in entropy (or a decrease in $-\overline{\Delta S}$). Probably the decrease in $-\overline{\Delta S}$ in the region around $n = 0.6$

is more rapid than it would have been if there were no transition to a mobile layer, and the small recovery up to n= 0.7 indicates a return to the normal change in entropy that occurs with adsorption in this region.

It is interesting to note that in this region, the swelling curve (Figure 8) observed by Collins (28) also changes, and the swelling increases more rapidly, presumably after the onset of the condensed film.

Thus, there are three distinct ranges over which the sorption process shows significant variations as reflected by the discontinuities in the - $\overline{\Delta S}$ plot;1)In the region from zero water content to the end of the B.E.T. range, which involves the formation of hydrogen bonds between water and the cellulose hydroxyls; 2) the formation of successive layers above the primary one, until the onset of a condensed film of water; and 3) the Harkins-Jura region which applies to condensed films. Similar results have been observed by Dunford and Morrison on silk fibroin (5), by Morrison and Hanlan on wool keratin (1). Some suggestion of a similar behaviour for the sorption of water by a number of proteins was made by Davis and McLaren (25).

The sorption of water vapour by cellulose results in the familiar sigmoid sorption isotherm, which shows a characteristic hysteresis. A very plausible explanation of sorption hysteresis is advanced by Barkas (11) who

postulates that the hysteresis is due to the plastic nature of hygroscopic materials such as cellulose (a manifestation of plasticity is that the stress-strain curve of a plastic body is different according as to whether the applied load is decreasing or increasing).

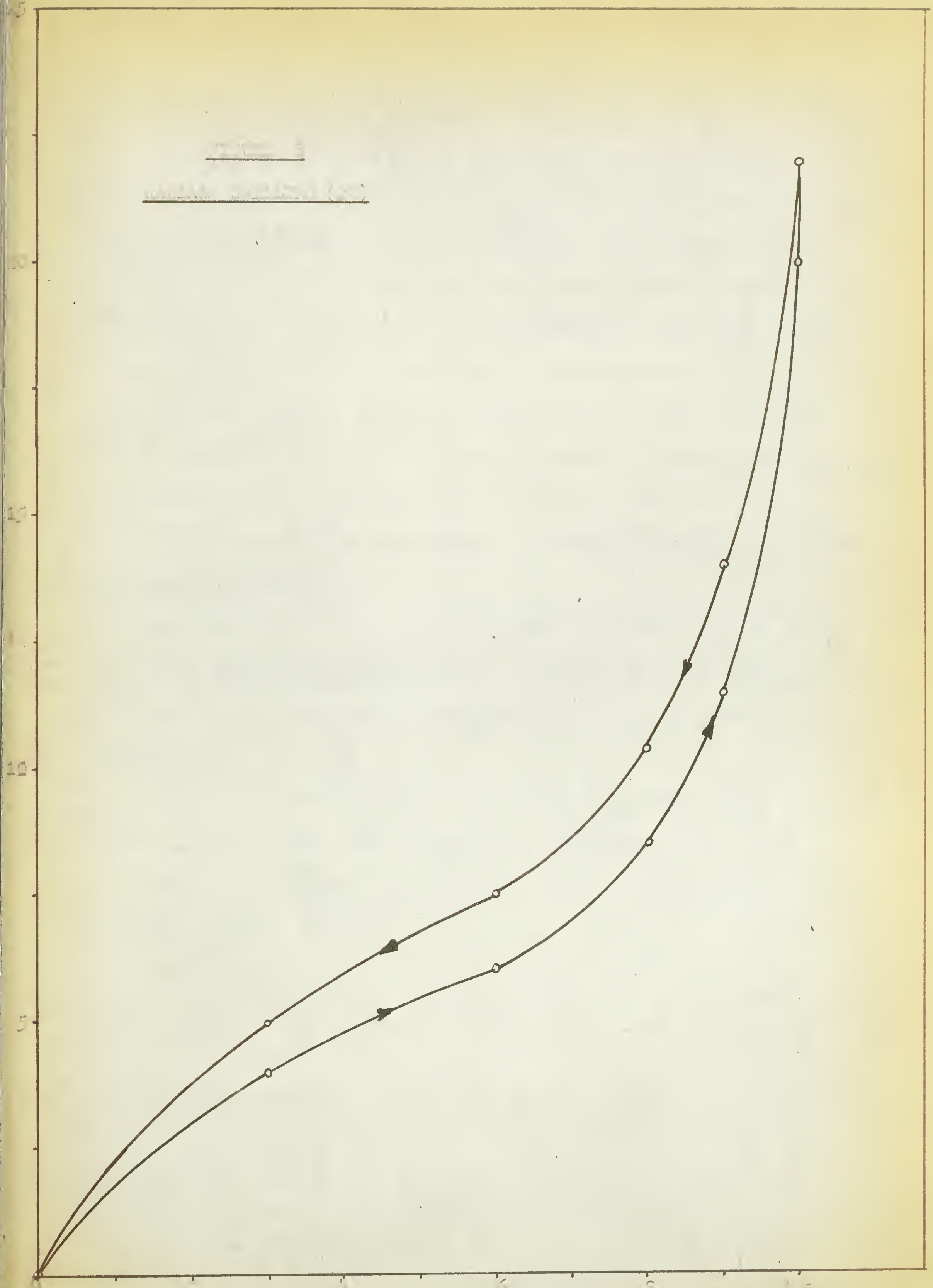
It would appear that the hysteresis is an entropy phenomenon. This is because the sorption isotherms are free energy curves and, since the enthalpies show no hysteresis and $\Delta F = \Delta H - T \Delta S$, therefore the hysteresis in ΔF is a reflection of a hysteresis in ΔS (and therefore $- \overline{\Delta S}$).

This observation is explained most satisfactorily by Barkas' suggestion. Thus, during adsorption of water (swelling), the stresses set up within the micelles of the cellulose disorganize the gel causing a decrease in the $- \overline{\Delta S}$, and during desorption (shrinkage), when the stress strain relations are different, organization occurs but not as rapidly as the disorganization. This sets up a different hydrostatic pressure which is reflected in a hysteresis of the vapour pressure. The effects of this are easily seen in the swelling curve (Figure 8) where we see that on the desorption side, a greater amount of swelling and hence of disorganization remains, resulting in a lower net negative entropy, than on the adsorption side as is seen in Figure 6.

Thus the swelling curve on desorption lies above, and the entropy curve on desorption lies below the corresponding adsorption branches.

Statistical treatments of the adsorption isotherm (22,24,27) have shown that the B.E.T. equation is based on the adsorption on localized sites rather than the formation of a mobile adsorbed monolayer. On the other hand, Harkins and Jura's interpretation of the adsorption isotherm is based on the assumption that a condensed film is formed. Thus one would expect the B.E.T. plot (Figure 7A) of the water vapour adsorption data to give a straight line plot up to a relative vapour pressure of 0.5. A plot of the Harkins-Jura (Figure 7B) gives a good straight line for relative vapour pressure greater than 0.5. Davis and McLaren (25) postulated a spectrum of sorption and chemisorption taking place, with chemisorption being the predominant effect at low water content.

It has been shown (4) that the Harkins-Jura equation fits the upper part of the adsorption isotherm, and that Liangs' (29) method can be used to correlate the B.E.T. and H.J. equations. As can be seen from Table 6, the monolayer contents given by the two equations are, within experimental error, the same.



25
20
15
10
5
0
.2
.4
.6
.8
1.0

Summary

The heats of wetting of cellulose in water at 25°C over the entire water content range have been determined. Thermodynamic functions have also been calculated, the differential heat and entropy curves indicate transitions from monolayer to multilayer formation and from the latter to a condensed film, which then becomes indistinguishable from liquid water. The magnitude of the energy requirements suggests that the chemisorption of hydrogen bond formation is an important effect at low water content.

Similar results have been observed for silk fibroin (5) and wool keratin (1).

Hysteresis in the sorption isotherm has been explained as an entropy phenomenon on the basis of Barkas' postulate of the plastic nature of hygroscopic materials such as cellulose.

Monolayer contents for the lower and upper regions of water content have been determined and agree well, thus supporting the correlation of the B.E.T. and H.J. equations through Liang's method.

Experimental Errors

The largest source of error in the experimental determination of the heat of wetting lay in the determination of the time of heating from the graph for the electrical duplication of the temperature rise (Figure 1). The reading of this graph was only to the nearest 5 seconds. This corresponds to a possible maximum error of 0.06 calories per gram. The Wheatstone bridge could be read to 0.1 ± .05 ohms. This corresponds to an error of ± 0.015 calories per gram in the heat of wetting. The sensitivity of the thermal to ambient temperature was 0.0002°C. per mm. scale deflection.

The heat capacity of the calorimeter plus the reaction cell has been previously calculated (1), as 111 cal/°C. Of this value approximately 80 cal/°C. were due to the calorimeter plus oil and 30 cal/°C to the reaction cell plus water.

A small correction of about .15 cal (as determined by a blank experiment) was applied owing to the dissipation, as heat, of the kinetic energy of the wetting liquid forced into the sample cell.

Bibliography

1. Hanlan, J.F., Master of Science Thesis, University of Alberta Library, 1957.
2. Morrison, J.L., and Hanlan, J.F., Nature, 179 528 (1957)
3. Dunford, H.B., Master of Science Thesis, University of Alberta Library, 1952.
4. Dunford, H.B., and Morrison, J.L., Can. J. Chemistry, 32 558 (1954).
5. Ibid, 33 904 (1955).
6. Bull, H.B., J.Am.Chem. Soc., 66 1499 (1944).
7. Dole, M., and McLaren, A.D., J. Am.Chem. Soc., 69 651 (1947).
8. Argue, G.H., and Maass, O., Can.J.Research, 12 564 (1935).
9. Wahba, M., Journal of Phys. and Colloid Science, 52 1197 (1948).
10. Ibid, 54 1148 (1950).
11. Barkas, W.W., Brit. Paper and Board Makers' Assoc., Proc., Tech. Sect. 36 421 (1955)
12. Rees, W.H., J. Textile Institute, 39 T351 (1948).
13. Guthrie, J.C., J. Textile Institute, 40 T489 (1949).
14. Wahba, M., and Nashed, S., Proc.Egypt. Acad. Sci., 8 128 (1953).
15. Wahba, M., and Nashed, S., J.Textile Institute, 48 T1 (1957).
16. Ott, E., Spurlin, H.M., and Graffin, M.W., *Cellulose and Cellulose Derivatives*, Interscience Publishers Inc., New York, 1954, Chapter II , IV, Volume 5.
17. Wiig, E.O., and Juhola, A.J., J. Am. Chem. Soc., 71 561 (1949).
18. Mann, J. and Marrinan, H. J., Trans. Faraday Soc., 52 481 (1956)

19. Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 60 309 (1938)

20. Harkins, W.D., and Jura, G., J. Am. Chem. Soc., 66 1366 (1944).

21. Urquart, and Williams, J.Text. Inst. 15 T559 (1924).

22. Hill, T.L., J. Chem. Phys. 14 263 (1946),
14 441 (1946),
15 767 (1947),
16 181 (1948).

23. Pauling, L., J. Am. Chem. Soc., 67 555 (1945).

24. Dole, M., J. Chem. Phys., 16 25 (1948).

25. Davis, S., and McLaren, A.D., J. Polymer Sci., 3 16 (1948).

26. Cassie, A.B.D. Trans. Faraday Soc., 41 458 (1945).

27. Ibid 43 615 (1947).

28. Collins, G.E., J. Text. Inst. 21 T311 (1930).

29. Liang, S.C., J. Phys. and Colloid Chem., 55 1410 (1951).

30. Brickman, W.J., Dunford, H.B., Tory, E.M., Morrison, J.L., Brown, R.K., Can. J. Chemistry 31 550 (1953).

B29778